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Title:

“Desulphurization of ferrous materials using sodium silicate”

Cross-reference to related applications: **None**

5 Federally sponsored statement: **N/A**

Reference listing: **None**

Description

FIELD OF THE INVENTION

The present invention relates to (1) the use of a sodium compound as the primary desulphurizing reactant in a reactive desulphurizing agent, (2) to an option of including other desulphurizing reactants obtained from other reactive alkali oxides, alkaline oxides or other chemical compounds and metallic solids, (3) the method for producing the sodium-based reactive desulphurizing agent, (4) the process of applying the sodium-based reactive desulphurizing agent to a molten ferrous material and (5) the process for the deoxidation or reduction of the iron oxide in a molten ferrous material.

BACKGROUND OF THE INVENTION

Ample agreement exists on the growing need for low sulphur steels. In most types of steels, the presence of sulphur above 0.015% is undesirable. The increasing stringent requirement for better desulphurization of steel is attributed to the need for producing high strength low alloy steel and steels resistant to hydrogen induced cracking. In addition, even minute contents of sulphur has pernicious effects on the manufacturing and finishing of steel products, such as brittle fractures in welding and fabrication, a tendency to separate along grain boundaries when stressed or deformed at temperatures near the melting point during the hot rolling phase in sheet steel processing, and even the influences on as-cast and the processing characteristics of the steel in terms of the workability of surface finish.

The desulphurizing of molten ferrous materials comprises thoroughly permeating the molten material with a reactive desulphurizing agent consisting of (1) metal oxides for replacing

the sulphur from the iron and for providing the flux required to float out the spent reactants and (2) the addition of solid metals to complete the deoxidization or reduction the iron. U.S. Pat. No. 4,014,685 teaches the four essential factors, for achieving good desulphurization in either a molten iron or steel, using a reactive desulphurizing agent. The factors are (1) high
5 desulphurizing agent basicity, (2) high temperature on desulphurizing agent contact with the molten material, (3) low oxygen potential and (4) high desulphurizing agent fluidity.

Furthermore, it has also been demonstrated that the rate of desulphurization increases when the molten metal and the reactive desulphurizing agent are strenuously agitated or perturbed to enhance the intimate contact between the reactive desulphurizing agent and the
10 molten metal. Prior art related to enhancement of the desulphurization process, U.S. Pat. No. 6,383,249, U.S. Pat. No. 5,021,986, U.S. Pat. No. 4,832,739, and U.S. Pat. No. 4,315,773, teaches the method of incorporating a gas-evolving component in the reactive desulphurizing agent. The gas-evolving component releases the gas at the moment the reactive desulphurizing agent comes in contact with the molten ferrous material.

15 The gas released in the interior of the molten ferrous material forms gas bubbles that expand rapidly under the effect of the increased temperature brought about by the contact of the reactive desulphurizing agent with the molten ferrous material. The gas bubbles, being of a lesser density, rise through the molten ferrous material. As the gas bubbles percolate or permeate through the molten, collisions take place between bubbles, and the colliding bubbles combine to
20 form bigger bubbles. In effect, the volume of the expanding gas bubbles provides the means for increasing the mobility or activity of the reactant metal oxides and also increases the contact area between the reactant oxides in the reactive desulphurizing agent and the molten ferrous material.

The increase in both, the mobility of the reactant oxides and the contact area, increases both the

rate of desulphurization and amount of sulphur removed from the molten ferrous material.

However, none of these examples given above advance the art of combining the gas-evolving compounds and the desulphurizing reactant compounds in reactive desulphurizing agent.

Over the past several decades, a multitude of methods and processes have been set forth
5 for the desulphurization of ferrous molten materials. Most of these methods are based on the reactions of a lime, fluorspar, aluminum oxide, alkali and alkaline metals or alloys, as well as the use of other reactants. An example of these methods is in U.S. Pat. No. 3,779,739, which teaches the art of desulphurization using calcium oxide and aluminum oxide or calcium oxide and calcium fluoride, wherein the calcium oxide increases the basicity of the desulphurizing agent
10 and the aluminum oxide and calcium fluoride increase the fluidity of the desulphurizing agent. Magnesium oxide has also been advanced in the art of desulphurizing ferrous materials, specifically metallic magnesium in U.S. Pat. No. 6,383,249.

Sodium, like magnesium, is a highly reactive metal, thus a high-performing desulphurizer that allows for a very high sulphur replacement in molten ferrous materials. However, because of
15 its high reactive property, metallic sodium is highly unstable at ambient temperatures and violently unstable at the temperatures of molten ferrous material and thus vaporizes quickly on contact with molten ferrous materials, hence metallic sodium, by itself, is ineffectual in removing sulphur. A preferred composition for the effective use of sodium as a desulphurizer is a chemical compound, such as in an oxidized state in combination with a flux-enhancing compound. A far-
20 reaching attractive feature in advancing the art of using sodium over magnesium as a desulphurizer is the availability of sodium compounds at a significantly lower cost.

The art of using sodium oxide, derived from sodium carbonate, as a reactant in a desulphurizing agent is described in U.S. Pat. No. 4,014,685, U.S. Pat. No. 4,956,010, and U.S.

Pat. No. 4,353,739. In none of these examples, where the art of using sodium oxide as a reactant in a reactive desulphurizing agent is put forth, is the art advanced wherein sodium silicate is used as the source of the sodium oxide desulphurizing reactant. Nor is a mention made on the preferred form for using a sodium silicate composition as the sole desulphurizer reactant in a desulphurizing agent.

SUMMARY OF THE INVENTION

A method is disclosed for removing sulphur in molten ferrous materials using a sodium-based reactant in a reactive desulphurizing agent. The preferred reactant in the reactive desulphurizing agent is sodium silicate. A lime, dolomite, an alumina or mixtures thereof, may optionally be added to enhance the replacement of the sulphur and control of the fluidity of the spent reactants in the molten ferrous materials.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

According to the present invention, a reactive desulphurizing agent is sodium silicate, wherein the chemical composition of the sodium silicate comprises of y parts of SiO_2 to x parts of Na_2O and wherein, yet further, the ratio, y/x , is anywhere from 0.5 to 5. The SiO_2 and the Na_2O are fused at high temperatures. In the preferred embodiment of the invention the fusion takes place in a glass tank at temperatures from 900 to 1500°C. Other types fusion units, such as a rotary furnace, can also be used for the present invention provided the end results are consistent with the intent and scope of the invention.

The sodium silicate reactive desulphurizing agent is combined with sulphur-laced molten ferrous materials. In the preferred embodiment of the invention, the molten ferrous material is

drawn, in predetermined amounts, and laid in a layer to cover the surface of a desulphurizing vessel. The layer of molten ferrous material is then covered by a predetermined amount of sodium silicate reactive desulphurizing agent. The process is repeated at least once until all the molten ferrous material available is desulphurized within the volume capacity of the vessel. As
5 the desulphurization of the molten ferrous materials progresses, the spent reactants fluidize the surface and are removed from the desulphurizing vessel. To complete the reduction or deoxidation of the iron, a metallic solid is introduced into the molten ferrous material. In the preferred embodiment of the invention the metallic solid is an aluminum rod.

In another embodiment of the invention, the reactants of the reactive desulphurizing
10 agent comprise: sodium silicate, as prepared in the preferred embodiment, and oxides of calcium, magnesium and aluminum. The preferred materials for said oxides are a lime compound such as limestone, dolomite and an alumina composite, respectively. The preferred composition of the reactive desulphurizing agent comprises:

Na_2O from about 4 to about 50%

15 SiO_2 from about 4 to about 50%

CaO is \leq 25%

MgO is \leq 4%

Al_2O_3 is \leq 14%

CO_2 is \leq 42%

20 The said preferred reactive desulphurizing agent composition is combined with the molten ferrous materials, using the procedure as described in the preferred embodiment of the

invention. On contact with the molten ferrous, the temperature of said reactive desulphurizing agent rises, causing the limestone and dolomite to release carbon dioxide gas into the molten ferrous material. As the carbon dioxide gas permeates through the molten ferrous material, the sulphur replacement activity of the metal oxide reactants is enhanced.

- 5 The released carbon dioxide gas forms bubbles within the molten ferrous material and rise to the surface of the desulphurizing vessel. As the gas rise through the molten ferrous material, the bubbles collide and combine to form bigger bubbles with increasing volumes. The increased gas volumes increase the surface area between the desulphurizing reactants and the molten ferrous material, thus increasing the amount and rate of sulphur replacement in the iron.
- 10 We suspect, that the rising bubbles of carbon dioxide contribute to the upward fluidity of the spent desulphurizing reactants, thus removing the sulphur from the iron and prevent the resulphurization of the ferrous material.

According to the invention, the preferred composition of the reactants in reactive desulphurizing agent, without the carbon dioxide comprises:

- 15 Na_2O from about 7 to about 50%
- SiO_2 from about 7 to about 50%
- CaO is \leq 45%
- MgO is \leq 8%
- Al_2O_3 is \leq 25%

- 20 These and other advantages and features of the present invention will be more fully understood with the examples thereof.

EXAMPLE 1

A reactive desulphurization agent, based on sodium, was prepared from a composition of a sodium silicate and oxides of aluminum, magnesium and calcium. The parts ratio of the silicon oxide to the sodium oxide was 2.3:1, resulting in a sodium silicate composition with about 29.7%, by weight, of sodium oxide and about 71.3%, by weight, of silicon oxide. In addition to the sodium silicate composition, alumina, dolomite and lime were added in the amounts given in Table 1. The components were combined using a blade mixer in three approximately equal batches to obtain consistent mixtures. The weight percentages of the oxides in the unspent reactive desulphurizing agent are listed in Table 2. After mixing, the components were placed in super-sacks and shipped to the site of the Basic Oxygen Furnace (BOF).

Table 1.

Desulphurizing Agent Component Weight	
Component	Kg
Sodium silicate	234.5
Alumina	284.1
Dolomite	218.8
Lime	535.4
Total	1272.8

Table 2

Desulphurizing Agent Composition (pbw)	
Reactive Oxides	
CaO	52.9%
Na ₂ O	6.2%
MgO	4.1%
Flux Enhancers	
Al ₂ O ₃	20.0%
SiO ₂	16.8%

Total 100.00%

At the BOF site, initially, 70 metric tons of molten steel were drawn into a tap vessel and
5 covered by 400 kg of the sodium-based reactive desulphurizing agent, as described in Table 1.
An additional 70 metric tons of molten steel were again drawn into the tap vessel and again
covered the sodium-based reactive desulphurizing agent. The controls parameters were
maintained constant to provide oxygen at 356ppm. A solid metallic aluminum wire was injected
into the molten steel to deoxidize the iron oxide, with the oxygen reduced to 2.5ppm. During the
10 desulphurization of the molten steel, neither the presence of toxic vapors nor the presence of
sodium where detected in the immediate surrounding area. The spent reactants of the reactive
desulphurizing agent remained dissolved and fluid during the desulphurization process.
Measurements performed on samples taken prior and after desulphurization indicate that the
sulphur content of the molten steel was reduced from 0.012% to about 0.00088%.

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EXAMPLE 2

In the second example, the sodium-based reactive desulphurizing agent based again was prepared from a sodium silicate and oxides of aluminum, magnesium and calcium. The parts ratio of the silicon oxide to the sodium oxide was maintained as before, 2.3:1, resulting in a sodium silicate composition with about 29.7%, by weight, of sodium oxide and about 71.3%, by weight, of silicon oxide. However the amounts the sodium silicate composition, alumina, dolomite and lime added were slightly change, as given by weight amounts in Table 3. As before, the components where combined using a blade mixer in successive batches. The batch weights for this example were not reported. The weight percentages of the oxide in the final sodium-based reactive desulphurizing agent composition are listed in Table 4. After mixing, the components were placed super-sacks and shipped to the BOF site.

Table 3

Desulphurizing Agent Component Weight	
Component	Kg
Sodium silicate	225.8
Alumina	364.8
Dolomite	200.9
Lime	408.5
Total	1200.0

Table 4

Desulphurizing Agent Composition (pbw)	
Reactive Oxide	
CaO	45.50%
Na ₂ O	7.00%
MgO	7.00%
Flux Enhancers	
Al ₂ O ₃	25.00%
SiO ₂	15.50%
Total	100.00%

Essentially the desulphurization procedure at the BOF site, as outlined in Example 1, was

5 repeated in this example, with the exception that the oxygen levels were lower both during the desulphurization phase and the deoxidation phase. Initially, 70 metric tons of molten steel were drawn into a tap vessel and covered by 400 kg of the sodium reactive desulphurizing agent, as described in Table 1. An additional 70 metric tons of molten steel were again drawn into the tap vessel and again covered with a layer of the sodium reactive desulphurizing agent. The controls

10 parameters were maintained constant to provide oxygen at 226ppm. Metal aluminum wire was injected into the molten steel to deoxidize the iron oxide. In this example, the oxygen was reduced to 1.7ppm. During the process, neither the presence of toxic vapors nor the presence of sodium were detected in the immediate surrounding area. The spent reactants of the reactive desulphurizing agent, as before, remained dissolved and fluid during the desulphurization

15 process. Measurements performed on samples taken prior and after desulphurization indicate that the sulphur content of the molten steel was reduced from 0.0153% to about 0.00135%.

A further variation of the process consists of a number of sequential charges of lesser amounts of the molten steel charge and provide said molten charge with a layer of the reactive desulphurizing agent, wherein each layer of the reactive desulphurizing is in intimate contact with the molten material.

- 5 It will be appreciated that the instant specifications and claims are set forth by way of illustrating and not limiting the present invention, and that various modifications and changes may be made without departing from the spirit, scope and intent of the present invention.